

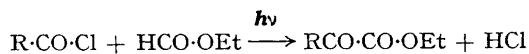
A New Synthesis of Ethyl Glyoxalates

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RECENTLY, we reported a novel one-step synthesis of substituted ethyl glyoxalates by means of photolysis of diethyl oxalate in various hydrogen-donating substrates.¹ Such synthesis, however,

has been somewhat limited by the reason that the substrate must be active to hydrogen abstraction. As an extension of our previous work, we report here the more convenient general method for the synthesis of the title compounds.



(Ia; R = Me) (IIa; R = Me)

(Ib; R = Et) (IIb; R = Et)

(Ic; R = Ph) (IIc; R = Ph)

Irradiation of acyl chlorides in ethyl formate gave the corresponding ethyl glyoxylates. All irradiations were carried out at room temperature, using a 120w low pressure mercury lamp as the light source. Product yields and irradiation time are given in the Table.

All products were identified by direct spectroscopic and gas-chromatographic comparisons with authentic samples. In the above ethyloxallylation, the substituted ethyl glyoxylates and hydrogen

chloride were always found as the principal products. In a consequence, it seems to be more likely that the main primary step may be the photodecomposition of acyl chloride to acyl and chloro-radicals.

TABLE

Acyl chloride	Irradiation time (hr.)	Recovered starting material	% (II) ^a
(Ia)	45	42.7	34.5
(Ib)	24	48.0	28.9
(Ic)	45	81.5	42.3

^a Figures in parentheses denote yield based on unrecovered starting material.

In addition, the desired ethyl glyoxylates were obtained, albeit in some lower yields, by the photolysis of several acyl nitriles in ethyl formate.

Studies on the scope and mechanism of this photoreaction are in progress.

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¹ Y. Odaira, T. Tominaga, T. Sugihara, and S. Tsutsumi, *Tetrahedron Letters*, 1964, 2527.